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Laser-Raman Study of Crystallinity Changes in Poly(ethylene Terephthalate)

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Synopsis

The bandwidth at one-half maximum intensity of the Raman-active C=O stretching vibration was found to correlate with density in poly(ethylene terephthalate). This correlation is valid for unoriented as well as highly oriented materials. It is suggested that a number of rotational states of the terephthalate segment occur in the amorphous polymer. Crystallization causes a resonance-stabilized planar conformation.

Introduction

In a recent paper, McGraw¹ reported on the Raman spectrum of poly(ethylene terephthalate) (PET). In particular, he studied the effects of high-temperature annealing on the Raman spectrum. The intensity of a band at 1096 cm^{-1} was found to correlate linearly with density. In making the measurement it was found necessary to use the band at 632 cm^{-1} in the PET spectrum as an internal intensity reference. The need for internal reference bands comes about since absolute Raman intensity measurements are difficult to make. Precise alignment of laser, sample, optics and monochromator is not reproducible from sample to sample. In using an internal reference, it must be certain that this Raman band is completely insensitive to the changes being studied in the polymer. Establishing the proper band for use as an internal reference may in itself require an absolute intensity measurement. It would be more desirable to have some alternate means for correlating the observed Raman spectra with changes in density or crystallinity.

Experimental

We have found a problem in using the relative intensity ratio of $1096\text{ cm}^{-1}/632\text{ cm}^{-1}$ for correlating with density. The correlation changes with orientation of PET. A plot of relative Raman intensity versus density is shown in Figure 1 for a series of heat-crystallized PET samples having no orientation. The same relative Raman intensity measurement was made on a series of PET fibers of differing draw ratio. The data for these drawn samples do not fall on the same line as the heat-crystallized samples. Clearly, the effect of molecular orientation as well as density

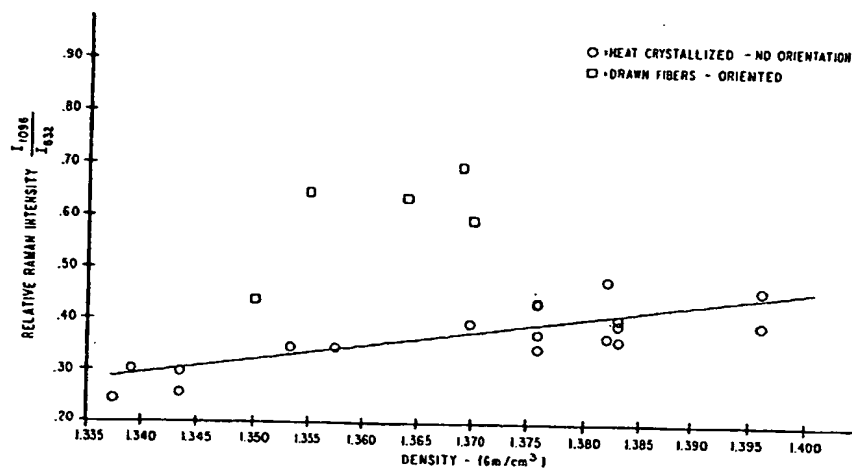


Fig. 1. Relative Raman intensity $I_{1096 \text{ cm}^{-1}}/I_{682 \text{ cm}^{-1}}$ vs. density.

or crystallinity plays a role in determining the Raman intensity. A similar conclusion was reached by McGraw² in his work with PET monofilaments.

Examination of the laser-Raman spectrum of 100% amorphous and highly crystalline PET in Figure 2 reveals two intense bands at 1618 and 1730 cm^{-1} . These bands are well separated from the remainder of the spectrum. The 1618 cm^{-1} band is assigned to a C—C vibration of the benzene ring while the band at 1730 is assigned to a C=O stretch.^{3,4} The bandwidth at one-half maximum intensity of the C=O stretching vibration at 1730 cm^{-1} was carefully measured for a large variety of PET samples. The width of the band at half-maximum was measured by drawing a baseline at the bottom of the band and measuring peak intensity.

Included in the PET samples were powders, unoriented heat crystallized filaments, yarns drawn and oriented above the glass transition temperature T_g and high-pressure crystallized material. These samples represented a collection having diverse morphology as well as differing orientation and crystallinity. Density measurements were made with density-gradient columns.

The Raman spectra were excited with 4880 Å radiation from an argon-krypton laser and dispersed by a Spex 1401 double monochromator. The mechanical slit width was held at 100 μ which represents a resolution at 1650 cm^{-1} of ca. 2 cm^{-1} ; the slit height was 2 mm. The Raman radiation was photon counted employing a cooled detector. Spectra were scanned at 10 $\text{cm}^{-1}/\text{min}$ in the region 1560–1750 cm^{-1} .

Figure 3 shows the Raman band at 1730 cm^{-1} for completely amorphous and >60% crystalline PET. The change in bandwidth is well above the resolution limits of the system. Similar examination of the band at 1618 cm^{-1} reveals no perceptible change in band contour or width.

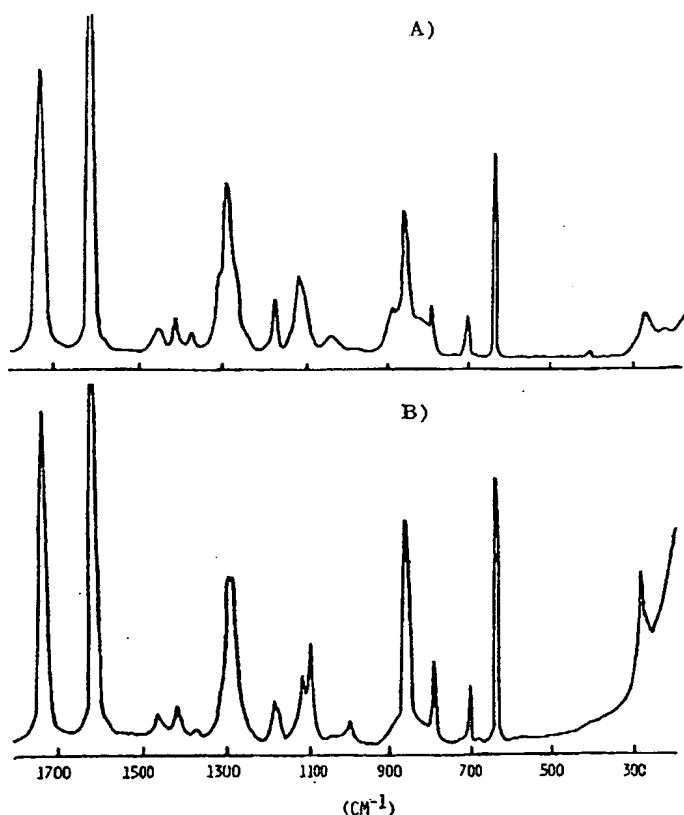


Fig. 2. Raman spectra of (a) amorphous PET and (b) partially crystalline PET.

Figure 4 is a plot of the bandwidth for the C=O stretching vibration versus measured density for the collection of samples. It may be seen that there is a linear correlation of bandwidth with density. The linear plot is the result of a multiple regression analysis which yielded a line:

$$\Delta\nu_{1/2} = 305 - 209\rho$$

where $\Delta\nu_{1/2}$ is the half-intensity bandwidth (cm^{-1}) and ρ is the density (g/cm^3).

This linear correlation of C=O bandwidth and density is independent of orientation effects in the sample. If constant amorphous density is assumed in partially crystalline PET, then the bandwidth may be used as a measure of crystallinity. This method requires no internal intensity standard and therefore requires no assumptions regarding band sensitivity to sample treatment. The measurement is also independent of orientation effects and may be used for any type of PET sample.

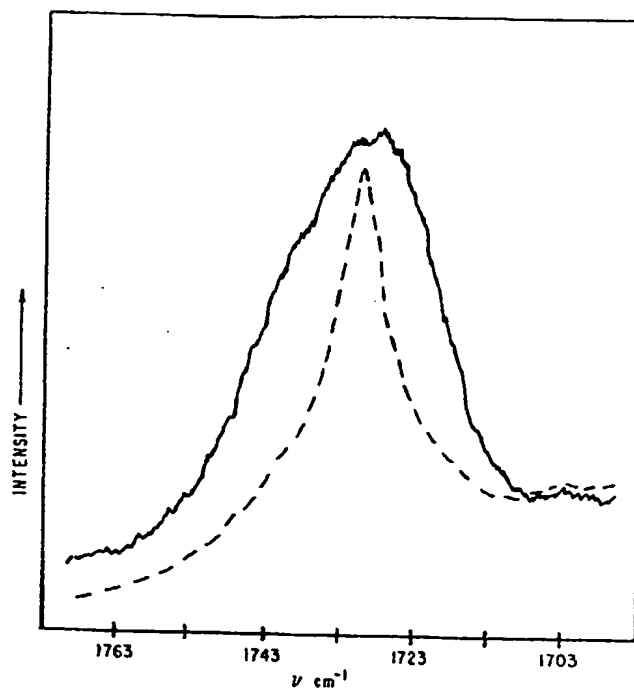


Fig. 3. Raman band of C=O Vibration at 1730 cm^{-1} : (—) amorphous PET; (---) crystalline PET.

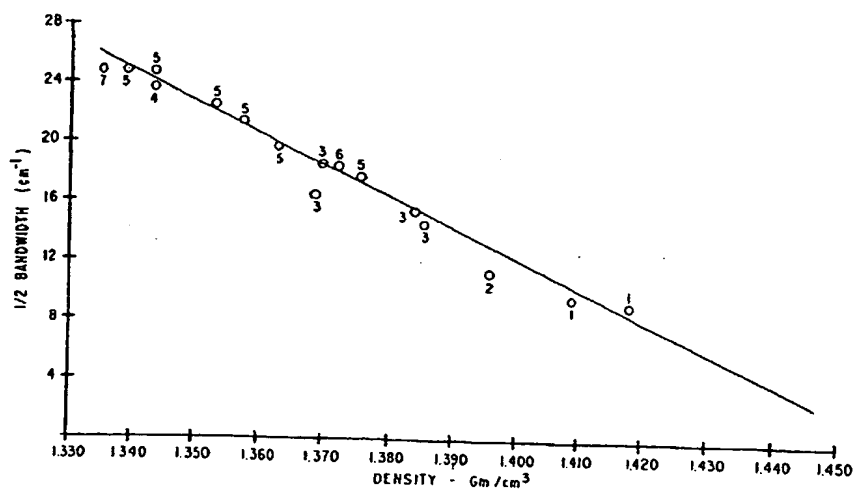
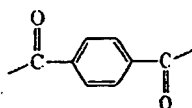


Fig. 4. Raman bandwidth at $1/2$ maximum intensity of C=O stretch vs. density: (1) high-pressure-crystallized rod; (2) filament heat-crystallized after long-term annealing below T_g ; (3) drawn yarn; (4) undrawn yarn; (5) heat-crystallized filament; (6) powder ground in liquid N_2 ; (7) amorphous filament.

The assumption of constant amorphous density in oriented samples may not be valid. Therefore, a measurement of crystallinity from total density or Raman bandwidth will not be precisely correct. The bandwidth measurement does, however, correlate well with total density whereas the Raman intensity does not for oriented samples. This correlation of Raman bandwidth with density independent of sample history is evidence that the bandwidth is a measure of total order in the system.

Discussion

The decrease in the C=O stretching vibration bandwidth with increasing density may be explained as follows. Manley and Williams, in an extensive study of the infrared spectra of PET⁶ and poly(cyclohexane 1,4-dimethylene terephthalate)⁶ assign the crystalline and amorphous spectra on the basis of a change in local symmetry of the terephthalate segment of the PET molecule. In crystalline PET the successive carbonyl groups on a benzene ring are in the *trans* conformation:



This molecular segment is said to exist in a planar conformation having D_{2h} symmetry. The authors claim a departure of the carbonyls from planarity with the benzene ring in the amorphous phase. There may be a rotation of the C—C=O bonds out of the benzene plane. This description

of the changes occurring on crystallizing PET is consistent with the Raman study.

We suggest that amorphous PET consists of a series of rotational states i.e., the carbonyls may be rotated out of the plane of the benzene ring by varying amounts. This distribution of rotational "isomers" would tend to cause a broadening of the C=O stretching band since each state would contribute its own C=O stretching frequency. When the PET is crystallized, the structure tends toward planarity and is resonance-stabilized. This becomes evident by a narrowing of the bandwidth of the C=O vibration. The fact that the C—C stretching vibration of the benzene ring at 1618 cm^{-1} has a bandwidth insensitive to crystallinity changes is consistent with this argument. Since the planar conformation is maintained for the benzene ring in all phases, it is not expected that the ring vibrations would interact in such a way as to alter their frequencies with changes in rotational states of the C=O groups.

An alternate possibility for the broader amorphous band has been suggested in a study of amorphous silicon.⁷ It is claimed that in amorphous material all vibrational modes can contribute to a Raman spectrum. This is unlike a crystal where only certain zone-center phonons contribute. The

broad amorphous band then represents a density of vibrational states. The fact that in PET only the C=O vibrational bandwidth changes with amorphous content indicates that this mechanism is probably not responsible for the band broadening.

Many previous vibrational spectroscopic studies⁸⁻¹⁶ have concentrated on describing the changes occurring in PET upon crystallization as due to rotational isomerism in the ethylene glycol portion of the molecule. From other suggestions in the literature^{2,4,5,17-19} as well as the present Raman study, it is clear that significant changes may occur in the terephthalate segment of PET during the amorphous to crystalline transition.

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